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(54) Continuous process for  
producing rubber-modified  
thermoplastic resins

(57) An impact-resistant resin is prepared by the continuous solution graft-polymerization of a monomer mixture comprising an alkenyl aromatic compound (e.g. styrene) and an alkenyl cyanide (e.g. acrylonitrile or methacrylonitrile) in the presence of an ethylene-propylene-non-conjugated diene rubber (EPDM) in an inert solvent comprising an aromatic hydrocarbon. Two or more polymerization vessels connected in series are used. The rubber is fed in the form of a homogeneous solution in

all or part of the monomers and/or the inert solvent to the first polymerization vessel, together with, if required, the remaining monomer or monomers and/or inert solvent. The rubber is kept in a dispersed state in the first polymerization vessel by stirring and the monomers are polymerized therein, with stirring, until 40—80 wt.% conversion of the monomers is achieved. The remaining monomer is polymerized, with stirring, in the second and, if appropriate, succeeding polymerization vessels until the polymerization is substantially complete. The products have excellent gloss, hardness, chemical resistance, weather resistance and impact resistance.

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**SPECIFICATION****Continuous process for producing rubber-modified thermoplastic resins**

The present invention relates to a process for producing rubber-modified thermoplastic resins and enables such resins to be produced with excellent weather resistance and impact resistance. In particular, the invention provides a continuous process for the solution graft-polymerization of a monomer mixture (comprising an alkenyl aromatic compound and an alkenyl cyanide) in the presence of an ethylene-propylene-nonconjugated diene terpolymer rubber (hereinafter referred to as "EPDM").

Compared with the so-called ABS resins (which are copolymers of an alkenyl aromatic compound and an alkenyl cyanide modified with an unsaturated rubber-like polymer, such as butadiene), the resins (AES resins) formed by replacing the unsaturated polymer in the ABS resins by an EPDM have improved weather resistance, this being a major disadvantage of ABS resins, whilst retaining the excellent properties characteristic of ABS resins.

A large number of proposals have been made, both in patents and in other literature, relating to the production of AES resins. At present, emulsion polymerization is generally used in the commercial production of ABS resins, but emulsion polymerization is not popular for preparing AES resins and bulk polymerization or solution polymerization prevail, since EPDM in the latex form is difficult to obtain and is costly.

Although many techniques have been disclosed for the production of AES resins, most of them are based on batchwise polymerization processes. In a solution polymerization process for the production of AES resins, since the reagent, solution is already viscous to some extent and hence the viscosity of the solution after completion of the reaction becomes very great, it follows that both feeding of the reagents to the polymerization vessel and discharge therefrom are difficult and time-consuming and, moreover, temperature control when heating or cooling during the progress of the polymerization becomes complicated, thus resulting in uneven product quality from batch to batch. Because of these problems, a batchwise polymerization process is not advisable for commercial scale production.

It is, therefore, desirable to provide a continuous polymerization process for the efficient production of AES resins and the technical development of such a process should be of great commercial importance. However, there is very little information available on such continuous processes.

Continuous solution polymerization processes for producing AES resins give rise to two important problems which differ from the problems arising in batchwise polymerization. One of the problems involves the grafting reaction and arises because there is a residence time distribution of reagents in continuous processes and the other involves phase transition (or phase separation) of the reagents.

The first problem arises because of the residence time distribution of reagents in the case of continuous polymerization, unlike the situation in batchwise polymerization where the whole of the polymerization system uniformly undergoes reaction and has an identical reaction history. It is well-known that, in a conventional continuous polymerization of monomers in a homogeneous system, the molecular weight distribution of the resulting high molecular weight polymer will vary, corresponding to a difference in the residence time distribution in the polymerization process. In the case of an AES resin, however, in addition to the resin-forming reaction (which gives rise to this molecular weight distribution) there also occurs a graft-polymerization reaction in which the resulting resin phase polymer is further grafted onto the EPDM and the way in which this is carried out greatly affects product quality. As a consequence, in a continuous polymerization process for producing an AES resin, the grafting degree distribution will vary depending upon the residence time distribution. In other words, the degree of grafting onto one EPDM molecule will differ from that onto another EPDM molecule or the grafting degree of one rubber particle is different from that of another rubber particle. For this reason, even if the average grafting degree has reached a certain desired level, there still remains a significant possibility that a portion of the resin will have an insufficient grafting degree. The resulting non-uniformity may adversely affect the impact resistance, chemical resistance and resistance to delamination of the resulting AES resin.

The second important problem relates to the phase transition or phase separation. When a solution polymerization process for producing a rubber-modified thermoplastic resin is carried out in a batchwise manner, it is conventional to feed the rubber into the polymerization vessel in the form of a homogeneous solution in a vinyl monomer and a solvent, the rubber is then allowed to separate from the solution in the course of the polymerization to form a discontinuous phase of rubber particles (this is the "phase transition").

Further polymerization and stirring gives the final dispersion state of the rubber particles. The same principle also applies to a solution polymerization process for the production of an AES resin. Even in a continuous polymerization process, phase transition can be caused at some stage of the polymerization because the polymerization system is in a phase equilibrium which is determined by the quantity of rubber, the quantity of the resin-phase polymer formed by polymerization, the quantity of solvent and the solubility parameters of each component in the polymerization system, as a result of this phase transition, a rubber particle dispersion can be obtained.

On the other hand, in batchwise polymerization, every portion of the polymerization system has

the same grafting degree before phase transition takes place and the whole system, having the same reaction history, is simultaneously subjected to phase transition. Moreover, the history of agitation before and after phase transition is the same for every portion of the system and hence particles of comparatively uniform size tend to be obtained, resulting in the product possessing good physical

5 properties. In contrast, in continuous polymerization, because of the influence of residence time distribution, the particles tend to become non-uniform in size and shape, they tend to have too large an average size and they may contain partially coarse particles. All of these give rise to inferior gloss and reduced hardness of fabricated articles made from the resulting polymer.

As a result of these problems, continuous solution polymerization for producing rubber-modified

10 thermoplastic resins involving a graft reaction and phase transition present great difficulties. Moreover, compared with ABS resins based on unsaturated rubber substrates, AES resins use as the substrate an EPDM, which has inferior compatibility with the resin phase, thus resulting in insufficient adhesion at the interface. In order to improve compatibility, it is necessary to increase the degree of grafting to a higher level than is required for ABS resins. It can, therefore, be seen that the manufacture of AES resins

15 by continuous polymerization involves still more difficult problems.

It has hitherto been generally accepted that, in batchwise polymerization, a reaction is first caused in a homogeneous solution and that the grafted high polymer formed by this reaction has good compatibility at the interface between the resin phase and the rubber particles, thus allowing interface energy to decrease. Hence, it seems that the grafted high molecular weight polymer acts as though it

20 were a surfactant to disperse the rubber in the form of relatively small particles. From these considerations, the importance of the reaction prior to phase transition has been generally recognized and, for these reasons, it has generally been considered desirable to carry out polymerization under such conditions that the polymerization system in the first polymerization vessel is prevented from undergoing phase transition and allowing the phase transition to take place in the second

25 polymerization vessel, alternatively, if phase transition is allowed to occur in the first polymerization vessel, polymerization conversion is kept as low as possible. Phase transition is prevented from occurring in the first polymerization vessel by maintaining a low polymerization conversion in that vessel, or by effecting the polymerization without stirring the system or by suitable selection of the type and quantity of solvent.

30 As a result of considerable study of continuous solution polymerization systems for the production of AES resins, we have found that, under the types of condition discussed above, it is only possible to obtain unsatisfactory results in terms of impact resistance, hardness, gloss and other properties of the polymer produced. However, we have surprisingly found that, if continuous polymerization is conducted whilst maintaining the polymerization conversion in the first polymerization vessel at a level much

35 higher than a certain critical value at which phase transition takes place (as shown hereafter in the Reference Example), it is possible to produce a resin having surprisingly good properties.

Thus, the present invention consists in a continuous solution polymerization process for producing a resin by the solution graft-polymerization of a monomer mixture comprising an alkenyl aromatic compound and an alkenyl cyanide in the presence of an ethylene-propylene-nonconjugated diene

40 rubber and in a solvent comprising an aromatic hydrocarbon, in which:

the polymerization is effected in two or more polymerization vessels connected in series;

said rubber is fed to the first polymerization vessel in the form of a homogeneous solution in all or part of said monomers and/or said inert solvent,

45 optionally, all or part of the remaining monomer or monomers and/or inert solvent are fed to the first polymerization vessel,

the rubber is dispersed in the first polymerization vessel and the monomers are polymerized, with stirring, until the polymerization conversion has reached a value from 40 to 80% by weight of the monomers; and

50 remaining monomers are polymerized, with stirring, in the subsequent polymerization vessel or vessels until polymerization is substantially complete: The resulting resin preferably contains from 5 to 30% by weight of the EPDM rubber.

Although the reasons why the process of the invention leads to the formation of a resin having excellent properties are unknown and although we do not wish to be limited by any theory, it is thought that the reason is as follows. A homogeneous solution of the starting material is fed to the first

55 polymerization vessel where the polymerization system is under such conditions of phase equilibrium that the EPDM in the feed solution must immediately precipitate. The precipitated EPDM is dispersed in the form of fine granules by vigorous stirring. Because of the large difference in phase equilibrium conditions between the feed solution and the polymerization system in the polymerization vessel and because of the large shear force exerted on the precipitated EPDM, there is almost instantaneously

60 formed a dispersion of EPDM particles having a small size and this dispersion is maintained throughout the course of the polymerization, leading to the production of a resin having good properties.

It has been found that, by carrying out the process of the invention, a sufficiently high degree of grafting can be achieved, even when no reaction takes place before the phase transition. Although the distribution of grafting degree of the resin produced according to the process of the invention cannot be

65 exactly confirmed (because of difficulties in its determination), the content of ungrafted EPDM in the

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polymerize has been found to be insignificantly small when determined by extraction with an aliphatic hydrocarbon solvent in which the ungrafted EPDM is soluble.

Furthermore, although rubber-modified thermoplastic resins manufactured by conventional solution polymerization processes have the disadvantage of a poor gloss (as is the case with AES resins), one of the advantages of the present invention is that it is possible to obtain an article having a high gloss even though the AES resin used is produced by a continuous solution polymerization process, provided that the process is carried out in accordance with the present invention. Although the factors affecting gloss are complicated, it is known that the most important factors are the particle size and particle size distribution of the rubber. In resins produced by the process of the invention, the particle size of the rubber seems to be sufficiently small and uniform. In fact, observation under an electron microscope revealed that the rubber particles have a substantially uniform size ranging from 0.3 to 0.7  $\mu$ .

Thus, it is possible to obtain by the process of the invention resins having well-balanced impact resistance and hardness, excellent resistance to weather and chemicals and a high gloss. Another advantage of the process of the invention is its high productivity.

EPDM rubbers suitable for use in the process of the invention preferably comprise ethylene and propylene in a weight ratio of from 90:10 to 20:80. The non-conjugated diene content is preferably in the range from 4 to 50, in terms of the iodine number. The non-conjugated diene may be any of the norbornenes (e.g. the alkenylnorbornenes and alkylidene-norbornenes), the cyclic dienes (such as dicyclopentadiene) and the aliphatic dienes (such as the hexadienes). The amount of EPDM used is preferably such that the rubber content of the final resin is from 5 to 30% by weight. The EPDM should be fed to the reaction system in the form of a homogeneous solution in a part or the whole of the monomers and/or the inert solvent. Preferably, the EPDM is dissolved in all or part of the alkenyl aromatic compound or in all part of the inert solvent or in a solution of the monomer or monomers in the inert solvent.

The alkenyl aromatic compound used as one of the monomers in the process of the invention is a compound in which an alkenyl group is attached to an aromatic group; the attachment is preferably such that the double bond of the alkenyl group is in a position for conjugation with the aromatic ring system and the alkenyl group is preferably a vinyl or vinylidene group. Examples of alkenyl aromatic compounds which may be used in the process of the invention are styrene and its derivatives, such as  $\alpha$ -methylstyrene, halogenated styrenes, 3,5-dimethyl-styrene and t-butylstyrene.

The alkenyl cyanide which is the other monomer for use in the process of the invention is a compound in which an alkenyl group is attached to a nitrile ( $-\text{C}\equiv\text{N}$ ) group and is preferably such that the double bond of the alkenyl group is in a position where it may conjugate with the bond of the nitrile group. The alkenyl group is preferably a vinyl or vinylidene group. Examples of suitable cyanides are acrylonitriles and its derivatives, such as methacrylonitrile.

A proportion of the alkenyl aromatic and alkenyl cyanide monomers can be replaced by other alkenyl (preferably vinyl or vinylidene) monomers, such as methacrylates and acrylates (e.g. methyl methacrylate or methyl acrylate), acrylic acid, methacrylic acid, acrylamide, methacrylamide, vinyl halides, vinyl ethers, maleic anhydride and other copolymerizable vinyl compounds. Where such other alkenyl monomers are used, the amount used is preferably up to 20% by weight, based on the total weight of the monomers. A preferred mixture is a combination of styrene with acrylonitrile in a weight ratio of from 90:10 to 60:40.

An essential component of the inert solvent used as the polymerization medium is an aromatic hydrocarbon. Suitable aromatic hydrocarbons include: benzene, toluene, ethylbenzene, xylene and isopropylbenzene. It is not objectionable to use up to 30% by weight (based on the total weight of the inert solvent) of polar solvents, such as ketones, esters, ethers, amides or halogenated hydrocarbons. However, the combined use of an aromatic hydrocarbon with an aliphatic hydrocarbon is undesirable. We prefer that the amount of inert solvent used should be from 50 to 200, more preferably from 60 to 200, parts by weight per 100 parts by weight of total EPDM plus monomers.

All with all solution graft-polymerization processes of the type of the present invention, it is normally necessary to employ a radical polymerization initiator. Although any radical initiator may be used, we prefer to use those organic peroxides known to be effective for graft polymerization, such as: the aromatic diacyl peroxides (e.g. dibenzoyl peroxide), the peroxyesters (e.g. t-butyl peroxyisobutyrate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxylaurate or t-butyl peroxylaurate or t-butyl peroxybenzoate); the peroxycarbonates (e.g. t-butyl peroxyisopropylcarbonate); or the ketone peroxides (e.g. 1,1-bis-t-butylperoxy-3,3,5-trimethylcyclohexanone).

It is not only possible but also sometimes preferable to use a combination of two or more of the above peroxides or to use one or more of the peroxides in combination with another radical initiator or to use different initiators in each polymerization vessel. In the first polymerization vessel, it is preferred to use at least one of the peroxide mentioned above. The amount of peroxide used should be such that the polymerization conversion in the first polymerization vessel is in the range of from 40 to 80% by weight of the monomers and this will depend upon the polymerization temperature, residence time and intended molecular weight of the polymer. However, in general, it is preferred to use from 0.1 to 2.0 parts by weight of peroxide per 100 parts by weight of total EPDM plus monomers.

The polymerization vessel may be of any type so long as it is provided with a suitable stirring mechanism, preferably an impeller capable of exerting a sufficient mixing and agitating effect throughout the whole polymerization system. At least two polymerization vessels should be used and should be connected in series. If only one polymerization vessel were used, a very long residence time would be required in order to achieve substantial completion of the polymerization and, even if a polymerization conversion of 40—80% or more were achieved, the resulting polymer would have inferior physical properties (as shown hereafter in Comparative Examples 4 and 5). In a continuous polymerization process, there occurs the residence time distribution previously described and a portion of the EPDM with a very small residence time may possibly remain ungrafted. The probability of this occurring is greatly reduced and the time required for substantial completion of the polymerization is also reduced by using a plurality of polymerization vessels connected in series. For this reason, we prefer to use 3 or 4 polymerization vessels connected in series. On the other hand, the use of too many polymerization vessels requires excessive investment for the construction of the plant and is undesirable from the economic as well as operational viewpoints. 5

When carrying out the process of the present invention, the polymerization conversion in the first polymerization vessel should be in the range of from 40 to 80% by weight based on the total monomers and is preferably from 50 to 75% by weight; the average degree of grafting is preferably controlled to be 30% by weight or more. The lower limit of 40% by weight on the polymerization conversion is required, since otherwise the impact resistance and gloss would deteriorate, as described previously. The upper limit on the polymerization conversion arises because of the important role played by the polymerization which occurs in the second and succeeding polymerization vessels, this polymerization has the effect of increasing the average grafting degree and decreasing the breadth of its distribution, as well as decreasing and making more uniform the particle size of the rubber dispersion formed in the first polymerization vessel. If the amount of residual monomer to be polymerized in the second and succeeding polymerization vessels is too small, it is clearly difficult to achieve these effects to any significant extent. Accordingly, the polymerization conversion in the first polymerization vessel should be maintained at a value not exceeding and preferably below 80% by weight. 10 15 20 25

Agitation is necessary in the second and succeeding polymerization vessels. The polymerization should be substantially completed (the term "substantial completion" as used herein means a final polymerization conversion of at least 85%, and preferably 90% or more, by weight). This is because the intended higher and uniform grafting degree as well as the smaller and uniform particle size described above are better attained by complete polymerization. 30 35

The feedstock used in the process of the present invention should be a homogeneous solution of the EPDM. It should be noted that alkenyl cyanide compounds do not, in general, dissolve EPDM rubbers. For instance, when preparing the rubber solution, if the proportion of alkenyl cyanide is large and the temperature is low, the rubber will be sparingly soluble. Alternatively, if an alkenyl cyanide is added to a homogeneous solution of the EPDM in an aromatic hydrocarbon, the EPDM will sometimes, depending upon the temperature and composition of the solution, precipitate. If a solution containing precipitated rubber is fed to the first polymerization vessel, a fine dispersion of rubber particles is not obtained and the polymer produced from such a heterogeneous solution will not have the desirable physical properties. 40 45

It is possible to feed a portion of the monomers and solvent to the second and succeeding polymerization vessels, provided that precautions are taken against disturbing the phase equilibrium, which would adversely affect the stability of the EPDM dispersion.

Selection of the polymerization temperature from the range of temperatures at which conventional radical polymerization can be carried out will depend upon the decomposition temperature of the initiator. With this proviso, however, the preferred temperature is in the range of from 60 to 150°C. It is possible, and may be desirable in some cases, to raise the temperature gradually from the first polymerization vessel to the last. 50 55

Recovery of the resin produced by the process of the invention, unreacted monomers and inert solvent from the polymerization mixture can be performed without the need for any special techniques, as is well-known in the art. Because of the economic advantages and uniformity of product quality characteristic of the continuous polymerization process carried out in accordance with the present invention, it is preferable to employ, if possible, a continuous method of recovery. An example of such a method is where volatile matter and resin particles are continuously recovered by means of a vent-type extruder, optionally after preliminary concentration by flash evaporation. 60

Although the resin obtained by the process of the invention already possesses excellent properties, there can be further incorporated, if necessary, conventional additives, for example: lubricants, such as liquid paraffin, fatty esters, fatty amides, metal salts of fatty acids or polysiloxanes; antioxidants of the phenol type, the amine type, the thioester type or the phosphorous acid ester type, and, if necessary, ultra-violet absorbers. These additives can be incorporated into the resin after its production or can be added to the polymerization system before or after polymerization. 65

The invention is further illustrated with reference to the following Examples in which the grafting degree was determined as follows:

1 g of resin was dissolved, with shaking, in 40 ml of methyl ethyl ketone (MEK) (24 hours) and the 65

mixture was twice centrifuged at 8,000 rpm for 30 minutes to collect the fraction insoluble in MEK. The acrylonitrile (AN) content was determined from the nitrogen content in the fraction and the grafting degree was calculated from the following equations, in which all percentages are by weight

$$A = \frac{[100 - \text{rubber content (\%)}] \times [\text{AN content (\%)} \text{ in MEK-insolubles}]}{\text{AN content (\%)} \text{ in total resin}}$$

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$$\text{Grafting degree (\%)} = \frac{A}{100 - A} \times 100$$

The rubber content was calculated from the polymerization conversion and the feed composition.

**EXAMPLE 1**

The polymerization apparatus used in this Example consisted of three polymerization vessels (polymerizers), each having a capacity of 30 litres and provided with a helical ribbon impeller, connected 10 in series. Polymerization was carried out under the conditions shown in Table 1 (which are also summarized in Table 2 in terms of parts by weight, the residence time given in Table 2 is an approximate value estimated by assuming the liquid specific gravity to be 0.87 g/ml). 10

TABLE 1

	Feeding rate (g/hour)	Polymerization temperature (°C)	Impeller speed (rpm)	Polymerization conversion (% by weight)
First polymerizer		80	60	52
EPDM	489			
Styrene	1940			
Acrylonitrile	831			
Toluene	2934			
t-Dodecyl-mercaptan	3.2			
BPO	13			
Second polymerizer		80	60	74
BPO	6.5			
Toluene	163			
Third polymerizer		80	60	88
BPO	6.5			
Toluene	163			
Exit of third polymerizer				
Irganox 1076	3.3			
Toluene	163			

Note:-

EPDM: JSR EP24 (a trade name of Japan Synthetic Rubber Co., Ltd.; termonomer: ethylenenorbornene, Mooney-viscosity ML<sub>1+4</sub><sup>100°C</sup> 65, Iodine number 15)

BPO: benzoyl peroxide

Irganox 1076: a registered Trade Mark of Ciba Geigy for antioxidant of phenol type.

EPO was fed as a 5% by weight solution in toluene through a separate pipe line. The other components were fed as a homogeneous solution at 60°C. The polymerization temperature was regulated by heating or cooling through a jacket. The feed entered each of the three connected

5 polymerization vessels from the bottom and was allowed to exit as an overflow from the top. After leaving the last of the polymerization vessels, the polymerization mixture was cooled down to 60°C, stored temporarily in a tank and sent directly to a three-vent extruder, 65 mm in diameter, where the volatiles were removed at 250°C, whilst the AES resin was recovered in the form of strand-cut pellets. Polymerization was carried out continuously for a period of 60 hours and the polymerization mixture 5

10 obtained towards the end of this period was subject to evaluation.

Test specimens were prepared by means of a 5 oz injection moulding machine (230°C) and tested for physical properties in a conventional manner. The results obtained are shown in Table 2, from which it can be seen that the melt fluidity, impact resistance and static strength are well-balanced and, in addition, the gloss is excellent. The model moulding test gave a product having a smooth surface

15 appearance and no appreciable delamination. Upon immersion in hexane at room temperature for 3 15

days, the weight increase was less than 1% by weight, extraction of the EPDM with hexane could not be detected and there was no noticeable change in appearance.

#### REFERENCE EXAMPLE

Using the same feed composition as in Example 1, a batchwise polymerization process was

5 conducted at 80°C in a 10 litre autoclave provided with a helical ribbon impeller. A sudden viscosity increase was observed at a polymerization conversion of about 18%, indicating that phase transition had occurred. From this observation, it is presumed that, in Example 1, the equilibrium point for the phase transition is at about 18% conversion. When one drop of the polymerization mixture from the first polymerization vessel in Example 1 was added to MEK and gently stirred, there appeared turbidity. A

10 portion of this polymerization mixture was also vacuum-dried and observed under an electron microscope using the osmium tetroxide-fixation technique. The rubber was found to have been dispersed in the form of granules.

#### EXAMPLES 2 to 11

A series of polymerization experiments were conducted following the procedure described in

15 Example 1, but under the conditions shown in Table 2.

In Examples 2 to 4, the type and amount of initiator and the polymerization temperature were varied. The results obtained were as good as those obtained in Example 1. In Example 5, using two initiators, the polymerization temperature was raised step-wise. In Example 6, the amount of EPDM rubber was different from that employed in the other Examples and a higher impact strength was

20 obtained. In Example 7, use was made, as the EPDM rubber, of JSR EP82 (in which the ter-monomer was dicyclopentadiene, Mooney viscosity 38; iodine number 10), this is a type of EPDM different from that used in the other Examples, but the results obtained were similar to those of the other Examples. In Example 8 MEK was used in combination with toluene and, in Example 9, ethyl-benzene was used as the solvent. In Example 10, methyl methacrylate (a vinyl monomer) was used in combination with the

25 other monomers, the resulting resin showed good properties, although these were somewhat different from the other resins in the balance of physical properties and in the colour.

All of the resins obtained in the Examples discussed above showed a good balance of melt fluidity, impact resistance and static strength. The delamination test and the hexane immersion test showed no problems.

30 In Example 11, two polymerization vessels were employed and the polymerization conditions were adjusted to comply with the requirements of the present invention by controlling the residence time. The physical properties of the resulting resin were as good as those of the resins obtained in the other Examples, except that a small amount of EPDM was found in the hexane extract.

#### COMPARATIVE EXAMPLE 1

35 Polymerization was carried out under the same conditions as in Example 1, except that a polymerization vessel having a capacity of 1.5 litres was used as the first polymerization vessel. In this vessel, the residence time was short, the polymerization conversion was low and phase transition did not take place. When a drop of the polymerization mixture was added to MEK, it coagulated into a mass which did not disperse, indicating that the rubber phase was continuous in the polymerization mixture.

40 The resulting resin had a low impact strength and very poor gloss.

#### COMPARATIVE EXAMPLE 2

Polymerization was carried out in the same manner as in Example 3, except that the initiator was divided into portions and only a small portion was added to the first polymerization vessel. In this vessel, although the phase transition was complete, the polymerization conversion was only 30% (i.e. lower than that required for the present invention). The resulting resin had inferior gloss.

#### COMPARATIVE EXAMPLE 3

A combination of benzoyl peroxide and dicumyl peroxide was used as the initiator, as in Example 5. The polymerization conversion in the first polymerization vessel was kept low by reducing the polymerization temperature. Results similar to those of Comparative Example 1 were obtained.

#### 50 COMPARATIVE EXAMPLE 4

Polymerization was carried out in a single polymerization vessel under the same conditions as prevailed in the first polymerization vessel of Example 3. The resulting resin had a markedly inferior impact strength and a low degree of grafting. Delamination was observed on subjecting a moulded specimen to flexure.

#### 55 COMPARATIVE EXAMPLE 5

As in Comparative Example 4, polymerization was carried out in a single polymerization vessel, but the residence time was prolonged and the temperature was somewhat higher to increase the polymerization conversion. The resin had a higher degree of grafting and a somewhat higher impact

strength than those of the resins produced in Comparative Example 4. However, delamination was considerable and some EPDM was extracted on immersion in hexane, suggesting the presence of rubber molecules of a low degree of grafting.

TABLE 2

		Example 1	Example 2	Example 3	Example 4	Example 5
Feed composition						
EPDM { Type	Quantity	Parts (wt.)	EP-24	EP-24	EP-24	EP-24
Styrene quantity	"	15	15	15	15	15
Acrylonitrile	"	59.5	59.5	59.5	59.5	59.5
Solvent { Type	Quantity	Toluene	25.5	25.5	25.5	25.5
Initiator { Type	Quantity	Toluene	Toluene	Toluene	Toluene	Toluene
Polymerizer (1st/2nd/3rd)						
Residence time	Hour	4.2 4.1 4	4 4 4	4 4 4	4 4 4	4 4 4
Temperature	°C	80 80 80	95 95 95	105 105 105	100 100 100	80 100 120
Conversion	%	52 74 88	62 85 92	67 88 92	65 84 93	52 88 96
Grafting degree	%	73	65	64	68	70
Physical property		(35 54 73)	(40 55 65)	(36 46 68)	(36 46 68)	(36 46 68)
Melt fluidity	$\times 10^{-3}$ ml/sec	16.0	11.0	8.3	8.0	14.0
Izod impact strength	notched kg.cm/cm	21.2	18.8	20.5	22.4	20.8
" (-30°C)	"	6.3	5.2	6.0	6.5	6.2
Rockwell hardness	R scale	100	103	104	105	103
Tensile strength	Kg/cm <sup>2</sup>	420	470	480	480	450
Tensile elongation	%	35	25	26	25	33
Gloss	%	82	84	83	85	78
Deflection temperature	°C	92	92	91	92	90

TABLE 2 (Cont'd)

		Example 6	Example 7	Example 8	Example 9
Feed composition					
EPDM { Type	Parts (wt.)	EP-24	EP-82	EP-24	EP-24
Styrene quantity	"	20	15	15	15
Acrylonitrile	"	56	59.5	59.5	59.5
Solvent { Type	Quantity	24	25.5	25.5	25.5
Initiator { Type	Quantity	Toluene	Toluene/MEK	Ethylbenzene	Ethylbenzene
Polymerizer (1st/2nd/3rd)	"	110	100	80/20	100
Residence time	Hour	PBZ	PBZ	PBZ	PBZ
Temperature	°C	4  4  4	4  4  4	4  4  4	4  4  4
Conversion	%	105 110 120	105 105 105	105 105 105	105 105 105
Grafting degree	%	62  89  97	64  86  92	68  88  94	63  82  91
Physical property					
Melt fluidity	$\times 10^{-3}$ ml/sec	9.8	9.5	7.8	12.0
Izod Impact strength	notched kg.cm/cm	33.2	17.3	21.2	19.3
" (-30°C)	R scale Kg/cm <sup>2</sup>	8.5	5.8	6.2	6.0
Rockwell hardness	"	93	107	107	104
Tensile strength	R scale Kg/cm <sup>2</sup>	410	500	500	470
Tensile elongation	%	30	25	26	25
Gloss	%	75	82	70	84
Deflection temperature	°C	89	92	91	91

TABLE 2 (Cont'd)

		Example 10	Example 11	Comparative Example 1	Comparative Example 2
Feed composition				EP-24	EP-24
EPDM { Type	Quantity	Parts (wt.)	15	15	15
Styrene quantity	"	"	50	59.5	59.5
Acrylonitrile	"	"	20 (MMA 15)	25.5	25.5
Solvent { Type	Quantity	Toluene		Toluene	Toluene
"	"	"	100	100	95/5
Initiator { Type	Quantity	PBZ		PBZ	PBZ
"	"	"	0.35	0.35	0.05 0.3
Polymerizer (1st/2nd/3rd)					
Residence time	Hour	4  4  4	6  6	0.2  4  4	4.1  4  4
Temperature	°C	105 105 105	105 105	105 105 105	105 105 105
Conversion	%	63  84  92	75  89	12  72  90	30  75  91
Grafting degree	%	66	66	68	64
Physical property					
Melt fluidity	$\times 10^{-3}$ ml/sec notched kg.cm/cm	14.5 18.8	10.0 20.4	8.0 12.0	19.8 15.2
Izod Impact strength	"	"	5.2	5.8	4.5
" (-30°C)	R scale	103	108	98	4.7
Rockwell hardness	Kg/cm <sup>2</sup>	420	490	380	100
Tensile strength	%	35	22	30	410
Tensile elongation	%	86	84	25	35
Gloss	%	88	92	58	58
Deflection temperature	°C			90	91

TABLE 2 (Cont'd)

		Comparativ Example 3	Comparative Example 4	Comparative Example 5
<b>Feed composition</b>				
EPDM { Type		EP-24	EP-24	EP-24
Quantity	Parts (wt.)	15	15	15
Styrene quantity	"	59.5	59.5	59.5
Acrylonitrile	"	25.5	25.5	25.5
Solvent { Type		Toluene	Toluene	Toluene
Quantity	"	100	100	100
Initiator { Type		BPO / FCD	PBZ	PBZ
Quantity	"	0.4/0.1	0.35	0.35
<b>Polymerizer (1st/2nd/3rd)</b>				
Residence time	Hour	4  4  4	40	12
Temperature	°C	60  90  120	105	110
Conversion	%	12  76  93	68	85
Grafting degree	%	70	40	62
<b>Physical property</b>				
Melt fluidity	×10 <sup>-3</sup> ml/sec	13.0	6.5	15.2
Izod impact strength	notched kg.cm/cm	14.0	3.2	8.3
" (-30°C)	"	2.5	1.5	2.5
Rockwell hardness	R scale	98	85	105
Tensile strength	Kg/cm <sup>2</sup>	380	320	480
Tensile elongation	%	30	15	15
Gloss	%	30	82	83
Deflection temperature	°C	89	89	91

**Note to Table 2:**

JSR EP-82: A trade name of Japan Synthetic Rubber Co. for EPDM (termonomer, dicyclopentadiene; Mooney viscosity, ML<sub>1+4</sub> 100°C, 38; Iodine number, 10)

PH3M : 1,1-Bis-t-butylperoxy-3,3,5-triethylcyclohexane

PBZ : t-Butyl peroxypbenzoate

PCD : Dicumyl peroxide

1) Melt fluidity: Rate of flow from a nozzle, 1 mm diameter × 2 mm length, of a "Koka Type Flow Tester" at 200°C under a load of 30 kg/cm<sup>2</sup>.

2) Izod impact strength: Notched specimen, 1/4 × 1/2 in. in cross-section; ASTM D 256 - 56

3) Tensile test: ASTM D638 - 617

4) Gloss: Reflectance at the specular direction; incident angle 45°; JIS Z 8741

5) Deflection temperature: ASTM D 648; 18.6 kg/cm<sup>2</sup>, not annealed.

## CLAIMS

1. A continuous solution polymerization process for producing a resin by the solution graft-polymerization of a monomer mixture comprising an alkenyl aromatic compound and an alkenyl cyanide in the presence of an ethylene-propylene-nonconjugated diene rubber and in a solvent comprising an aromatic hydrocarbon, in which:  
 5       the polymerization is effected in two or more polymerization vessels connected in series;  
       said rubber is fed to the first polymerization vessel in the form of a homogeneous solution in all or part of said monomers and/or said inert solvent;  
       optionally, all or part of the remaining monomer or monomers and/or inert solvent are fed to the  
 10      first polymerization vessel;  
       the rubber is dispersed in the first polymerization vessel and the monomers are polymerized, with stirring, until the polymerization conversion has reached a value of from about 40 to 80% by weight of the monomers; and  
       remaining monomers are polymerized, with stirring, in the subsequent polymerization vessel or  
 15      vessels until polymerization is substantially complete.  
 2. A process according to Claim 1, in which there are employed 3 or 4 polymerization vessels connected in series.  
 3. A process according to Claim 1 or Claim 2, in which the monomers are polymerized in the first polymerization vessel until the polymerization conversion reaches a value of from 50 to 75% by weight.  
 20      4. A process according to any one of the preceding Claims, in which the final polymerization conversion is 90% or more by weight.  
 5. A process according to any one of the preceding Claims, in which the polymerization is effected at a temperature of from 60 to 150°C.  
 6. A process according to any one of the preceding Claims, in which said rubber has an ethylene to propylene weight ratio of from 90:10 to 20:80 and a non-conjugated diene content of from 4 to 50 in terms of iodine number.  
 25      7. A process according to any one of the preceding Claims, in which said non-conjugated diene is a norbornene, a cyclic diene or an aliphatic diene.  
 8. A process according to any one of the preceding Claims, in which said alkenyl aromatic compound is a vinyl aromatic or vinylidene aromatic compound.  
 30      9. A process according to Claim 8, in which said alkenyl aromatic compound is styrene,  $\alpha$ -methylstyrene, a halogenated styrene, 3,5-dimethylstyrene or t-butyl-styrene.  
 10. A process according to any one of the preceding Claims, in which said alkenyl cyanide compound is a vinyl or vinylidene cyanide compound.  
 35      11. A process according to Claim 10, in which said alkenyl cyanide compound is acrylonitrile or methacrylonitrile.  
 12. A process according to any one of the preceding Claims, in which said monomer mixture additionally contains a methacrylate, an acrylate, acrylic acid, methacrylic acid, acrylamide, methacrylamide, a vinyl halide, a vinyl ether or maleic anhydride.  
 40      13. A process according to any one of the preceding Claims, in which the aromatic hydrocarbon employed as solvent is benzene, toluene, ethylbenzene, a xylene or isopropylbenzene.  
 14. A process according to any one of the preceding Claims, in which said inert solvent comprises up to 30% by weight of a ketone, an ester, an ether, an amide or a halogenated hydrocarbon.  
 45      15. A process according to any one of the preceding Claims, in which the polymerization is effected in the presence of at least one radical polymerization initiator which is an aromatic diacyl peroxide, a peroxyester, a peroxy carbonate or a ketone peroxide.  
 16. A process according to any one of the preceding Claims, applied to the production of a resin having a rubber content of from 5 to 30% by weight.  
 50      17. A process according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.  
 18. A resin when produced by a process according to any one of the preceding Claims.